Electrophoretic Deposition for Improved Trace Element Homogeneity in Silica Reference Materials

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Introduction and Motivation

- Reproducible calibration measurements depend on homogeneous reference materials. We developed glassy reference standards using electrophoretic deposition (EPD) to consolidate doped SiO_2 nanoparticles, achieving better platinum group element homogeneity than in available standards.[1]
- While EPD is attractive for making fully custom reference materials, we aim in this work to further validate our method by analyzing two sets of new EPD samples. For a control, equivalent samples were compressed mechanically by die-pressing (DP).
- Spatially resolved techniques such as laser ablation mass spectrometry can quantitatively characterize heterogeneity in spatial dopant distribution.

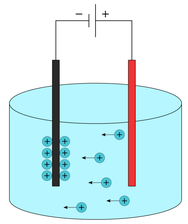

Figure 1. This depiction of EPD shows positively charged particles drifting in suspension to deposit on the anode of a circuit with applied current.[2]

Sample Images and Description

- Samples were fabricated from SiO_2 nanoparticle feedstocks (Fig. 2, top images). The particles were doped with ~1 ppm of over 40 trace elements from Li to U.
- One EPD and one DP sample from each feedstock were analyzed. Set 1 uses partial additions of silica precursor (Fig. 3, L) while Set 2 uses one addition of the same total amount. Thus, EPD and DP can be intercompared with Set 1 and Set 2 (Fig. 4, R).

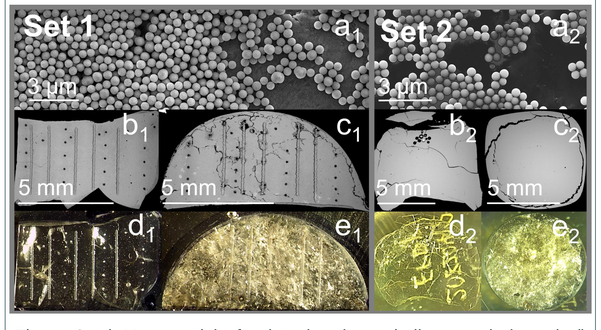

Figure 2. a) Nanoparticle feedstocks show similar morphology. b,d) EPD samples. c,e) DP samples. b,c) Backscattered electron images, showing little macroscopic variation in Z contrast. d,e) Optical images with laser tracks/spots seen in Set 1 (Set 2 was not yet ablated); EPD samples are transparent while DP has ubiquitous microstructure.

Experimental Methods

The following steps summarize the experiment.
1 through 4: Sample Production and Preparation
5 through 7: Measurement and Data Analysis

1. **Generate** feedstocks via the Stöber process[3]
2. **Consolidate** samples using either EPD or DP
3. **Densify** by sintering in a reducing environment
4. **Mount** in epoxy and polish flat for analysis

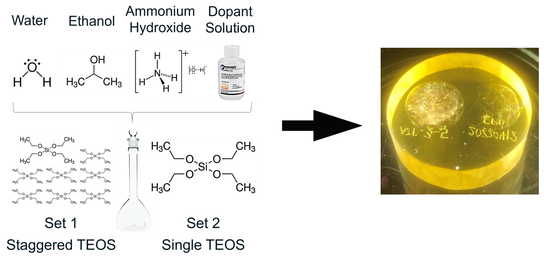

Figure 3. Step 1 into Step 4. Particle feedstock materials (L) and Set 2 samples (R), mounted and polished. TEOS is tetraethyl orthosilicate, a silica precursor which provides Si to the SiO_2.[4-9].

5. **Measure** all samples with LA-ICP-MS
6. **Calculate** relative standard deviation (RSD) of counts measured at locations across the surface
7. **Evaluate** performance of each synthesis (Set 1 vs. Set 2) and consolidation method (EPD vs. DP)

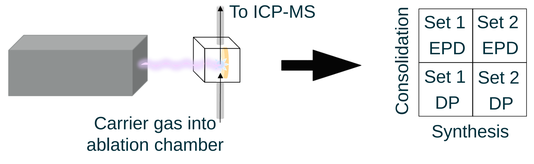

Figure 4. Step 5 into Step 7. Mounted samples are measured with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to quantify spatial uniformity of dopant distribution.

Set	Laser	ICP-MS
1	Applied Spectra J200 λ = 266 nm; 5 ns pulse width; 8 Hz rep rate; 4% laser power	Thermo Scientific iCAP TQ 100 ms dwell time; KED mode w/ He cell gas
2	Teledyne Analyte G2 λ = 193 nm; 10 ns pulse width; 10 Hz rep rate; 3 J/cm² fluence; 150 pulses per dose	Agilent 7500x 100 ms dwell time; KED mode w/ He cell gas

Table 1. Sets 1 and 2 were measured separately. Instrument model and available parameters used for each set are given here.

Results

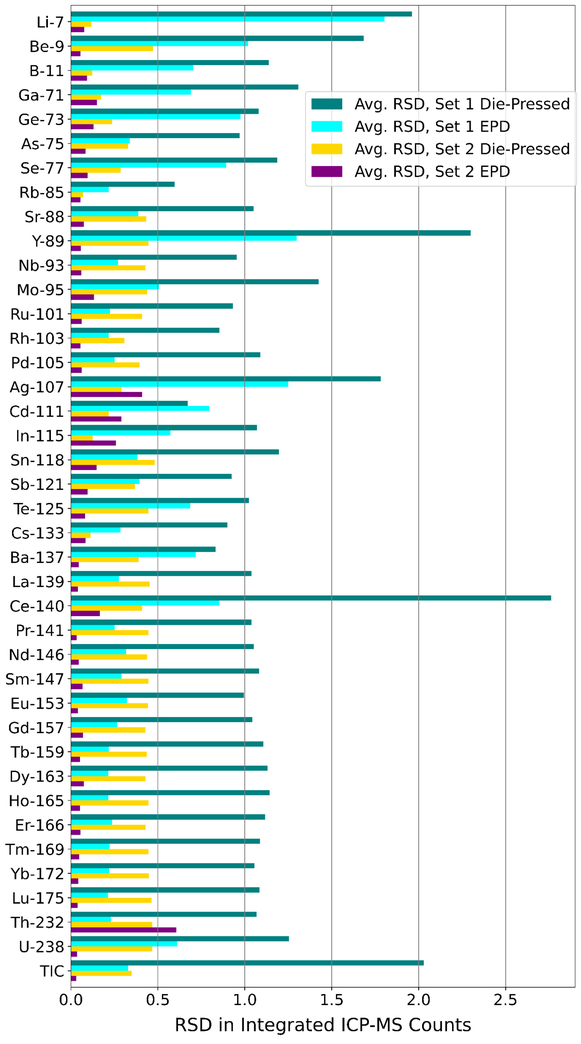

Table 2. One isotope of each of 39 elements and the total ion count (TIC) are considered. The RSD in spatially-resolved integrated LA-ICP-MS counts is reported for each elements across 4 samples.

- The lowest RSD (0.03) was observed for ^{141}Pr in the Set 2 EPD sample, which exhibited RSD ≤ 0.10 for 29 of 39 elements. By contrast, the lowest Set 1 RSD was 0.21 (^{163}Dy, ^{165}Ho, ^{175}Lu), also seen in EPD.
- Only 4 analytes (^{107}Ag, ^{111}Cd, ^{115}In, and ^{232}Th) showed an RSD worse in EPD than in DP. The remaining 35 showed lower RSD in EPD samples.

Discussion

- Generally, the dopant heterogeneity in both Sets 1 and 2 was greatly improved in EPD samples relative to DP. Although this result supports the hypothesis that EPD is driving this effect, the mechanism of action is not yet well understood.
- The difference between Set 1 and Set 2 was also significant beyond the trend in observed EPD effects, with Set 2 generally favored. This outcome motivates the adoption of a synthesis like the one used for Set 2 in fabricating future samples.

Conclusions

- A trend in improved homogeneity of spatial dopant distribution was observed in EPD samples versus DP, with observed RSD as low as 0.03. EPD shows potential as a new method of fabricating customizable glassy reference materials for use in method development and QC applications.
- Confirmatory measurements are warranted using a compatible technique beyond LA-ICP-MS, such as secondary ion mass spectrometry (SIMS). Like LA-ICP-MS, SIMS is a spatially resolved technique which benefits from homogeneity in reference materials. Nanoscale SIMS imaging may be able to elucidate informative microstructural features.
- Additional parameter space in the fabrication of this type of sample is open to exploration, in steps such as sintering and even the EPD process itself.

References and Acknowledgments

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[6] Texas Scientific Products, ICP-MS Complete Standard (43 Elements)
[7] Fisher Scientific, volumetric flasks
[8] Sigma-Aldrich, tetraethylorthosilicate
[9] Vedantu.com, the correct electron dot structure of water

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